PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| Applicant's or agent's file reference | FOR FURTHER ACTION | see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |
|---|---|---|
| P18142A/B0U | | |
| International application No. | International filing date *(day/month/year)* | (Earliest) Priority Date *(day/month/year)* |
| PCT/GB 98/ 01597 | 01/06/1998 | 31/05/1997 |
| Applicant | | |
| GILTECH LIMITED et al. | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   - [ ] the text is approved as submitted by the applicant
   - [X] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:
   Figure No. ---
   - [ ] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 98/01597

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

There is provided a method for forming a water-soluble glass fibre or wool. The method comprises heating the glass composition above its melting point to produce a molten glass and then cooling the molten glass slowly to a pre-selected working temperature at which the fibres will be drawn. Suitable working temperature include those in a range of 400 to 1000° C. The working temperature will usually be at least 200°C lower than the temperature to which the molten glass is heated above its melting point and may be 50-300°C above the Tg of the glass. Phosphorous pentoxide is suitable as a glass former and B203 may be present as an additive. Optionally the glass may release silver ions, e.g. by addition of silver orthophosphate during manufacture of the glass.

# INTERNATIONAL SEARCH REPORT

[redacted]tional Application No
PCT/GB 98/01597

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 C03C13/00 C03B37/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 578 023 A (CORNING INC) 12 January 1994<br>see page 4, line 20 - page 5, line 34;<br>claim 4; tables I-III | 1-6 |
| A | WO 86 04807 A (UNIVERSITY OF DAYTON, US)<br>28 August 1986<br>cited in the application<br>see claims 1-5 | 1 |
| A | WO 92 07801 A (ZIMMER INC) 14 May 1992<br>cited in the application<br>see claims 1,7,8 | 1 |

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 21 August 1998 | 02/09/1998 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Stroud, J |

1

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/01597

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | DATABASE WPI<br>Section Ch, Week 08<br>Derwent Publications Ltd., London, GB;<br>Class D22, AN 83-18194K<br>XP002075169<br>& JP 58 004 821 A (MITSUBISHI MINING & CEMENT CO) , 12 January 1983<br>see abstract | 1 |
| A | DATABASE WPI<br>Section Ch, Week 25<br>Derwent Publications Ltd., London, GB;<br>Class L01, AN 73-80941U<br>XP002075170<br>& JP 48 042 814 B (NIPPON SHEET GLASS CO LTD) , 1973<br>see abstract | |

1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/01597

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0578023 A | 12-01-1994 | US 5330940 A | 19-07-1994 |
| | | CA 2084471 A | 07-01-1994 |
| | | JP 6056472 A | 01-03-1994 |
| WO 8604807 A | 28-08-1986 | US 4604097 A | 05-08-1986 |
| | | AU 5518386 A | 10-09-1986 |
| | | EP 0211942 A | 04-03-1987 |
| | | JP 7005335 B | 25-01-1995 |
| | | JP 62501905 T | 30-07-1987 |
| WO 9207801 A | 14-05-1992 | US 5215563 A | 01-06-1993 |
| | | AU 658380 B | 13-04-1995 |
| | | AU 8952991 A | 26-05-1992 |
| | | CA 2094931 A | 02-05-1992 |
| | | EP 0555390 A | 18-08-1993 |
| | | JP 6504754 T | 02-06-1994 |

# PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

## PCT

### NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

| | |
|---|---|
| **Date of mailing** (day/month/year)<br>14 January 1999 (14.01.99) | |
| **International application No.**<br>PCT/GB98/01597 | **Applicant's or agent's file reference**<br>P18142A/BOU |
| **International filing date** (day/month/year)<br>01 June 1998 (01.06.98) | **Priority date** (day/month/year)<br>31 May 1997 (31.05.97) |
| **Applicant**<br>GILCHRIST, Thomas et al | |

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   21 December 1998 (21.12.98)

   [ ] in a notice effecting later election filed with the International Bureau on:

   _____

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
|---|---|
| **The International Bureau of WIPO**<br>**34, chemin des Colombettes**<br>**1211 Geneva 20, Switzerland** | Authorized officer<br>Nicola Wolff |
| Facsimile No.: (41-22) 740.14.35 | Telephone No.: (41-22) 338.83.38 |

# PATENT COOPERATION TREATY



# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| Applicant's or agent's file reference | FOR FURTHER ACTION | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
|---|---|---|
| P18142A/PKE/BOU | | |
| International application No. | International filing date *(day/month/year)* | Priority date *(day/month/year)* |
| PCT/GB98/01597 | 01/06/1998 | 31/05/1997 |
| International Patent Classification (IPC) or national classification and IPC | | |
| C03C13/00 | | |
| Applicant | | |
| GILTECH LIMITED et al. | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

| Date of submission of the demand | Date of completion of this report |
|---|---|
| 21/12/1998 | - 6. 09. 99 |
| Name and mailing address of the international preliminary examining authority: | Authorized officer |
| European Patent Office<br>D-80298 Munich<br>Tel. +49 89 2399 - 0 Tx: 523656 epmu d<br>Fax: +49 89 2399 - 4465 | Ritter, R<br><br>Telephone No. +49 89 2399 8578 |

Form PCT/IPEA/409 (cover sheet) (January 1994)

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/01597

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-17 as originally filed

**Claims, No.:**

1-10 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|---|---|---|---|
| Novelty (N) | Yes: | Claims | 9,10 yes |
| | No: | Claims | 1-8 no |
| Inventive step (IS) | Yes: | Claims | 9,10 yes |
| | No: | Claims | 1-8 no |
| Industrial applicability (IA) | Yes: | Claims | 1-10 yes |
| | No: | Claims | |

2. Citations and explanations

**see separate sheet**

1)Reference is made to the following documents:

~~D1: EP-A-0578023~~

D2: WO 86 04807 (cited in the application page 3, line 5)

D3: WO 9207801 (cited in the application page 3, line 22).

2) The present application does not fulfil the requirements of Article 33(2) PCT:
The subject-matter of claims 1-8 of the present application is known from D1( page 2, lines 49-56; page 4, line 20 -page 5, line 34; claim 4; tables I-III).
Also the subject-matter of D2 (claims 1-5) and D3 (claims 1,7,8) is novelty destroying for claim 1 of the present application.

3) None of the cited documents discloses or suggests a method wherein a silver ion releasing glass is manufactured (claims 9, 10 of the present application).

*The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:*

IPEA/ US

# PCT

**CHAPTER II**

## DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

| Identification of IPEA | Date of receipt of DEMAND |
|---|---|
| | |

**Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION**

Applicant's or agent's file reference: LE9-99-029

| International application No. | International filing date *(day/month/year)* | (Earliest) Priority date *(day/month/year)* |
|---|---|---|
| | 26 October 2000 (26.10.00) | 29 October 1999 (29.10.99) |

Title of invention:

INK COMPOSITIONS CONTAINING ULTRAVIOLET ABSORBERS

**Box No. II APPLICANT(S)**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

Lexmark International, Inc.
IP Law Dept.
740 West New Circle Road
Lexington, KY 40550
US

Telephone No.: 859-232-7843
Facsimile No.: 859-232-7850
Teleprinter No.:

| State *(that is, country)* of nationality: | State *(that is, country)* of residence: |
|---|---|
| US | US |

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

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TC 1700 MAIL ROOM

| State *(that is, country)* of nationality: | State *(that is, country)* of residence: |
|---|---|
| | |

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

| State *(that is, country)* of nationality: | State *(that is, country)* of residence: |
|---|---|
| | |

☐ Further applicants are indicated on a continuation sheet.

Sheet No. 2

International application No.

**Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**

The following person is [X] agent [ ] common representative

and [X] has been appointed earlier and represents the applicant(s) also for international preliminary examination.

[ ] is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

[ ] is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

DASPIT, Jacqueline M.
Lexmark International, Inc.
Intellectual Property Law Dept.
740 West New Circle Road
Lexington, KY 40550
US

Telephone No.: 859-232-7843

Facsimile No.: 859-232-7850

Teleprinter No.:

[ ] **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**

**Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

[X] the international application as originally filed

the description: [X] as originally filed; [ ] as amended under Article 34

the claims: [X] as originally filed; [ ] as amended under Article 19 (together with any accompanying statement); [ ] as amended under Article 34

the drawings: [X] as originally filed; [ ] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. [ ] The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

**Language for the purposes of international preliminary examination:** English

[X] which is the language in which the international application was filed.

[ ] which is the language of a translation furnished for the purposes of international search.

[ ] which is the language of publication of the international application.

[ ] which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

**Box No. V ELECTION OF STATES**

The applicant hereby **elects all eligible States** *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes **not to elect:**

Sheet No. 3

International application No.

**Box No. VI CHECK LIST**

| The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination: | | | | For International Preliminary Examining Authority use only: received | not received |
|---|---|---|---|---|---|
| 1. translation of international application | : | 0 | sheets | ☐ | ☐ |
| 2. amendments under Article 34 | : | 0 | sheets | ☐ | ☐ |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | 0 | sheets | ☐ | ☐ |
| 4. copy (or, where required, translation) of statement under Article 19 | : | 0 | sheets | ☐ | ☐ |
| 5. letter | : | 0 | sheets | ☐ | ☐ |
| 6. other (*specify*) | : | 0 | sheets | ☐ | ☐ |

The demand is also accompanied by the item(s) marked below:

1. [X] fee calculation sheet
2. [ ] separate signed power of attorney
3. [X] copy of general power of attorney; reference number, if any:
4. [ ] statement explaining lack of signature
5. [ ] nucleotide and or amino acid sequence listing in computer readable form
6. [ ] other (*specify*):

**Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

*Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).*

Jacqueline M. Daspit, Agent

**For International Preliminary Examining Authority use only**

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. [ ] The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. [ ] The applicant has been informed accordingly.
4. [ ] The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. [ ] Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

**For International Bureau use only**

Demand received from IPEA on:

CHAPTER II

# PCT

## FEE CALCULATION SHEET

**Annex to the Demand for international preliminary examination**

| | |
|---|---|
| International application No. | For International Preliminary Examining Authority use only |
| Applicant's or agent's file reference LE9-99-029 | Date stamp of the IPEA |

Applicant

LEXMARK INTERNATIONAL, INC.

**Calculation of prescribed fees**

| | | |
|---|---|---|
| 1. Preliminary examination fee ..... | 490.00 P | |
| 2. Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)* ..... | 153.00 H | |
| 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box..... | USD 643.00 TOTAL | |

**Mode of Payment**

| | | | |
|---|---|---|---|
| [X] | authorization to charge deposit account with the IPEA (see below) | [ ] | cash |
| [ ] | cheque | [ ] | revenue stamps |
| [ ] | postal money order | [ ] | coupons |
| [ ] | bank draft | [ ] | other *(specify)*: |

**Deposit Account Authorization** *(this mode of payment may not be available at all IPEAs)*

The IPEA/ US [X] is hereby authorized to charge the total fees indicated above to my deposit account.

[X] *(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

| 12-1213 | 7 May 2001 | |
|---|---|---|
| Deposit Account Number | Date *(day/month/year)* | Signature |

# PCT

## GENERAL POWER OF ATTORNEY

*(for several international applications filed under the Patent Cooperation Treaty)*

(PCT Rule 90.5)

The undersigned person(s)
*(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

Lexmark International, Inc.
740 West New Circle Road
Lexington, KY 40550
US

hereby appoints (appoint) the following person as: ☒ agent ☐ common representative

**Name and address**
*(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

MCARDLE, John J.; PEZDEK, John V.; BRADY, John A.; LAMBERT, D. Brent; SANDERSON, Michael T.; DASPIT, Jacqueline M.; MORGAN, Deborah E.; JACOBS, Elizabeth C.
Lexmark International, Inc.
740 West New Circle Road
Lexington, KY 40550
US

to represent the undersigned before

☒ all the competent International Authorities
☐ the International Searching Authority only
☐ the International Preliminary Examining Authority only

in connection with any and all international applications filed by the undersigned with the following Office

RO/US as receiving Office

and to make or receive payments on behalf of the undersigned.

**Signatures of the applicant(s)** *(where there are several persons, each of them must sign; next to the signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading this power):*

Vincent J. Cole, Vice President, General Counsel and Secretary

V. J. Cole

Date: 5-15-01

Form PCT/Model of general power of attorney (for several international applications)(July 1992)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C03C 13/00, C03B 37/02

A1

(11) International Publication Number: WO 98/54104

(43) International Publication Date: 3 December 1998 (03.12.98)

(21) International Application Number: PCT/GB98/01597

(22) International Filing Date: 1 June 1998 (01.06.98)

(30) Priority Data:
9711178.5 31 May 1997 (31.05.97) GB

(71) Applicant *(for all designated States except US)*: GILTECH LIMITED [GB/GB]; 12 North Harbour Estate, Ayr KA8 8AA (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GILCHRIST, Thomas [GB/GB]; 67 Midton Road, Ayr KA7 2TW (GB). HEALY, David, Michael [IE/GB]; Midton House, By Alloway KA7 4EZ (GB).

(74) Agent: OUZMAN, Beverley; Murgitroyd & Company, 373 Scotland Street, Glasgow G5 8QA (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

**Published**
*With international search report.*

(54) Title: METHOD OF PRODUCING WATER–SOLUBLE GLASS FIBRES

(57) Abstract

There is provided a method for forming a water–soluble glass fibre or wool. The method comprises heating the glass composition above its melting point to produce a molten glass and then cooling the molten glass slowly to a pre–selected working temperature at which the fibres will be drawn. Suitable working temperature include those in a range of 400 to 1000 °C. The working temperature will usually be at least 200 °C lower than the temperature to which the molten glass is heated above its melting point and may be 50–300 °C above the Tg of the glass. Phosphorous pentoxide is suitable as a glass former and B203 may be present as an additive. Optionally the glass may release silver ions, e.g. by addition of silver orthophosphate during manufacture of the glass.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **AL** | Albania | **ES** | Spain | **LS** | Lesotho | **SI** | Slovenia |
| **AM** | Armenia | **FI** | Finland | **LT** | Lithuania | **SK** | Slovakia |
| **AT** | Austria | **FR** | France | **LU** | Luxembourg | **SN** | Senegal |
| **AU** | Australia | **GA** | Gabon | **LV** | Latvia | **SZ** | Swaziland |
| **AZ** | Azerbaijan | **GB** | United Kingdom | **MC** | Monaco | **TD** | Chad |
| **BA** | Bosnia and Herzegovina | **GE** | Georgia | **MD** | Republic of Moldova | **TG** | Togo |
| **BB** | Barbados | **GH** | Ghana | **MG** | Madagascar | **TJ** | Tajikistan |
| **BE** | Belgium | **GN** | Guinea | **MK** | The former Yugoslav Republic of Macedonia | **TM** | Turkmenistan |
| **BF** | Burkina Faso | **GR** | Greece | | | **TR** | Turkey |
| **BG** | Bulgaria | **HU** | Hungary | **ML** | Mali | **TT** | Trinidad and Tobago |
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"Method of Producing Water-Soluble Glass Fibres"

The present invention relates to a method for the production of water soluble glass fibres and glass wool.

It is known that certain glasses, in which the usual glass former, silicon dioxide, is replaced with phosphorous pentoxide, are soluble in water and body fluids. The rate of dissolution is controlled largely by the addition of glass modifiers such as calcium oxide. In simple terms, the greater the concentration of the modifier the slower the rate of dissolution. The rate of dissolution may range from minutes through to several years.

Soluble phosphate based glasses which have demonstrated good biocompatability can incorporate inorganic metals such that a sustained release of the metals can be provided at the wound site. Such materials can also find use in mechanical applications where, for example, slow release of an anti-corrosion agent may be beneficial.

Certain applications require that the glass is in the

form of wool or fibres for mechanical applications such as insulation wool and packaging. Thus, for example, Mohr et al in "Fibre Glass" (Van Norstrand, Reinhold Company, New York 1978) and Jaray in "A New Method of Spinning Glass Fibres" (28th Annual SPI RP/C Institute proceedings 1973, Section 3-A) describe the production of wool and fibres, respectively, from molten glass. The glass fibres can be used for insulation, construction or even communication purposes. Glass wool also finds uses in packaging and insulation applications.

Normally, glass fibres are produced from molten glass using traditional fibre pulling techniques; whereby filaments of high temperature molten glass (850°-1300°C) are formed into strands and stretched over pull rolls before being collected onto a reel.

Glass wool formation is similar in that the glass is initially melted in a crucible. The crucible has suitable apertures to allow filaments of glass to flow downwards, which are then "blown" into wool using jets of either steam or compressed air. Alternatively, glass wool can be formed using a flame attenuation process, developed by Owens-Corning Fibreglass Corporation circa 1940. In this process molten glass passes through a bushing stage where primary filaments approximately 1 mm wide are formed. The fibres are then aligned into an exact uniformly juxtaposed array, using a fibre guide, into a jet flame issuing from an internal combustion burner. The jet flame causes thinning and lengthening of the fibres before they are collected on a steel mesh belt.

In both cases, the glass is either supplied in molten form direct from a crucible or from a temperature-

gradient furnace.

Generally, water soluble glasses do not lend themselves to these traditional fibre and wool forming techniques. As an example, US Patent 4,604,097 of Graves et al discloses a water soluble drawn fibre, composed primarily of calcium oxide and phosphorous pentoxide. The fibre produced has a very low tensile strength, compared to fibres spun from non-soluble glass compositions.

Further, water soluble glasses can also be chemically aggressive when molten, unlike traditional glasses where silicon dioxide is used as the glass former. Additionally, the fibres produced are prone to thermal shock and can suffer from devitrification or crystallisation.

To combat problems of devitrification and crystallisation, water soluble glass fibres have been previously produced in exacting conditions. Thus, for example, Zimmer et al in WO92/07801 discloses drawing fibres from a water soluble glass composed primarily of phosphorus pentoxide, calcium oxide and iron oxide. In order to keep the viscosity of the glass suitable for drawing, the fibres were drawn at 1200°C. Also as a result of the chemically aggressive nature of the glass at that temperature the glass was pulled in an oxygen rich atmosphere (as high as 80% oxygen by volume). Obviously the commercial production of glass fibres under these high temperature controlled atmospheric conditions is expensive.

The problems of working with water soluble glass are compounded by the very nature of the glass. Metal oxides of elements such as lead and tellurium have

previously been used in glass as additives to affect qualities of the glass; crystallisation temperature, viscosity and density, for example. As a result of environmental concerns and particularly when the glasses are to be used in a biological application these additives must be avoided and replaced by more acceptable alternatives.

Therefore, it is an object of the present invention to provide environmentally acceptable water soluble glass fibres with suitable mechanical properties, and to produce said fibres under less forcing conditions.

The present invention provides a method for forming a water-soluble glass fibre and/or glass wool, the method comprising producing a water-soluble glass and heating said glass above its melting point to form molten glass, cooling at least a portion of said molten glass to a pre-selected working temperature and then processing said molten glass having said working temperature into fibres and/or wool.

Generally, the glass is initially heated to a melting temperature of 500°-1200°C, preferably 750°-1050°C. The temperature is then slowly lowered to the working temperature at which fibre formation occurs.

Generally, the working temperature of the glass will be at least 200°C lower than the temperature at which the glass is initially heated. Suitable working temperatures may fall within the following ranges 400°-500°C, 500°-900°C (preferably 550°-700°C, more preferably 550°-650°C, especially 600°-650°C) and 800-1000°C. The working temperature selected will depend upon the glass composition, but an approximate indication of a suitable working temperature can be

established as hereinafter described. Depending upon the glass composition used, the working temperature may be a range of suitable temperatures. The range of working temperatures may be narrow, for example of only 10°C, so that fibre formation may occur only between the temperature of N°C to (N+10)°C. Other glass compositions may have a wider temperature range for the working temperature in which glass formation is possible.

Alternatively, the working temperature of the glass may be defined as 50-300°C above the Tg of the glass.

In order to obtain an approximate indication of the working temperature for any particular glass composition, the glass composition should be slowly heated to its melting point. As soon as the glass is molten, frequent attempts to pull the composition upwardly to form a fibre should be made, with the temperature of the composition being very gradually increased between attempts. The temperature range of the composition during which fibre formation is possible should be noted and used as a preliminary working temperature in the process of the invention.

It will be clear to those skilled in the art that the pulling speed at which the fibre is drawn off can affect the choice of working temperature and the diameter of the fibre required. Where a fibre of relatively large diameter is required, the fibre tends to be pulled more slowly and the working temperature may need to be decreased slightly. Where a fibre of relatively small diameter is required (eg a glass wool), the fibres may be drawn at the much higher pulling speed and the working temperature may need to be increased (thus lowering the viscosity of the

composition to accommodate the increased pulling speed). Selection of the exact working temperature in respect of any particular fibre size and composition will be a simple matter of routine evaluation of optimal process conditions.

With reference to the "working temperature" of the glass, the skilled person will appreciate that the furnace temperature may differ considerably from the temperature of the glass itself and indeed there may be a significant temperature gradient in the glass. Ideally the "working temperature" will be the temperature of the glass as fibre formation (ie. pulling) takes place. In many compositions however, it may not be practical to measure the temperature at the surface of the glass where pulling occurs by insertion of a temperature probe as the introduction of the probe may precipitate crystallisation of the glass. One alternative is to place a temperature probe into the bushing and to monitor the bushing temperature which will be a good indicator of the glass temperature at the moment of fibre formation. Alternatively an Infra Red pyrometer may be focused onto the appropriate area of the glass and used to monitor the temperature.

The glass to be formed into fibres will generally be heated until molten, optionally clarified, and then cooled slowly and controllably until the appropriate working temperature is reached and fibre formation can commence. The initial heating of the glass above its melting point and the subsequent fibre formation may be carried out in a single vessel or, alternatively, the molten glass may be transferred to a vessel designed specifically for fibre formation. One way of holding the molten glass in a vessel having a bushing within its lower surface until the temperature drops to the

required working temperature is to coat or fill the holes of the bushing with a material that gradually melts over the period of time taken for the glass to reach the temperature required.

The most important aspect of the present invention is the manner in which the working temperature is reached. We have found that the molten glass, which may preferably be heated significantly above its melting point, should be allowed to cool in a highly controlled manner, the temperature being only gradually reduced until the working temperature is reached. A stirrer may be present to ensure that the temperature of the whole of the molten glass is kept as uniform as possible.

The glass is cooled to a temperature at which the glass will not crystallise for at least the period of time needed to convert the melt to fibre. This temperature is termed a "holding temperature". The rate of cooling from this holding temperature is determined by the rate at which the melt is consumed at the bushing and the difference in temperature between the bushing temperature (the working temperature) and the melt holding temperature.

Due to low viscosity and narrow temperature band for many of these compositions, control of the balance between melt temperature, bushing temperature and glass throughput rate is critical.

According to a further aspect of the present invention there is provided a composition suitable for processing into glass fibres and/or wool.

Phosphorous pentoxide ($P_2O_5$) is preferably used as the

glass former.

Generally the mole percentage of phosphorous pentoxide in the glass composition is less than 85%, preferably less than 60% and especially between 30-60%.

Alkali metals, alkaline earth metals and lanthanoid oxides or carbonates are preferably used as glass modifiers.

Generally, the mole percentage of alkali metals, alkaline earth metals and lanthanoid oxides or carbonates is less than 60%, preferably between 40-60%.

Boron containing compounds (eg $B_2O_3$) are preferably used as glass additives.

Generally, the mole percentage of boron containing compounds is less than 15% or less, preferably less than 5%.

Other compounds may also be added to the glass to modify its properties, for example $SiO_2$, $Al_2O_3$, $SO_3$, sulphate ions ($SO_4^{2-}$) or transition metal compounds (eg. first row transition metal compounds).

Typically the soluble glasses used in this invention comprise phosphorus pentoxide ($P_2O_5$) as the principal glass-former, together with any one or more glass-modifying non-toxic materials such as sodium oxide ($Na_2O$), potassium oxide ($K_2O$), magnesium oxide (MgO), zinc oxide (ZnO) and calcium oxide (CaO). The rate at which the glass dissolves in fluids is determined by the glass composition, generally by the ratio of glass-modifier to glass-former and by the relative proportions of the glass-modifiers in the

glass. By suitable adjustment of the glass composition, the dissolution rates in water at 38°C ranging from substantially zero to 25mg/cm$^2$/hour or more can be designed. However, the most desirable dissolution rate R of the glass is between 0.01 and 2.0mg/cm$^2$/hour.

The water-soluble glass is preferably a phosphate glass, and preferably comprises a source of silver ions which may advantageously be introduced during manufacture as silver orthophosphate ($Ag_3PO_4$). The glass preferably enables controlled release of silver and other constituents in the glass and the content of these additives can vary in accordance with conditions of use and desired rates of release, the content of silver generally being up to 5 mole %. While we are following convention in describing the composition of the glass in terms of the mole % of oxides, of halides and of sulphate ions, this is not intended to imply that such chemical species are present in the glass nor that they are used for the batch for the preparation of the glass.

The optimum rate of release of silver ions into an aqueous environment may be selected by circumstances and particularly by the specific function of the released silver. The invention provides a means of delivering silver ions to an aqueous medium at a rate which will maintain a concentration of silver ions in said aqueous medium of not less than 0.01 parts per million and not greater than 10 parts per million. In some cases, the required rate of release may be such that all of the silver added to the system is released in a short period of hours or days and in other applications it may be that the total silver be released slowly at a substantially uniform rate over a

period extending to months or even years. In particular cases there may be additional requirements, for example it may be desirable that no residue remains after the source of the silver ions is exhausted or, in other cases, where the silver is made available it will be desirable that any materials, other than the silver itself, which are simultaneously released should be physiologically harmless. In yet other cases, it may be necessary to ensure that the pH of the resulting solution does not fall outside defined limits.

Generally, the mole percentage of these additives in the glass is less than 25%, preferably less than 10%.

Embodiments of the invention will be described with reference to the following non-limiting examples.

**Example 1**

| | Component | Mole % |
|---|---|---|
| Glass Composition | | |
| | $Na_2O$ | 31.05 |
| | CaO | 16.00 |
| | $Ag_2O$ | 3.88 |
| | $P_2O_5$ | 46.08 |
| | $Na_2PO_3F$ | 0.97 |
| | $2Al_2O_3.B_2O_3$ | 2.00 |

100 grams of the sample was heated to 900°C before being cooled and pulled at 650°C, at 25 km/hr. Overall the fibre was good; one sample was 10 km in length and 11 grams in weight, although there was some crystallisation at the pulling temperature.

**Example 2**

| | Component | Mole % |
|---|---|---|
| Glass Composition | | |
| | $Na_2O$ | 29.51 |
| | CaO | 15.21 |
| | $Ag_2O$ | 3.68 |
| | $P_2O_5$ | 43.80 |
| | $2Al_2O_3.B_2O_3$ | 1.90 |
| | $Na_2PO_3F$ | 1.90 |
| | $Na_2B_4O_7.10H_2O$ | 1.00 |
| | $Na_2PO_4$ | 3.00 |

74 grams of the sample was heated to 1000°C before being cooled and pulled at 635°C at 25 km/hr. The fibre produced was ultrafine; one sample was 18 km in length and 59 grams in weight. The sample was sprayed with WD40 to prevent water absorption and to aid lubricity. There was some debris at the bottom of the crucible, but this was found to be just iron deposits from the brushing rod.

**Example 3**

| | Component | Mole % |
|---|---|---|
| Glass Composition | | |
| | $Na_2O$ | 34.20 |
| | CaO | 16.15 |
| | $P_2O_5$ | 44.65 |
| | $Na_2SO_4$ | 5.00 |

200 grams of the sample was heated to 1050°C before being cooled and pulled at 635°C at 25 km/hr. The fibre was good although there was some crystallisation at the pulling temperature.

**Example 4**

| | Component | Mole % |
|---|---|---|
| Glass Composition | | |
| | $Na_2O$ | 32.40 |
| | CaO | 15.30 |
| | $P_2O_5$ | 42.30 |
| | $2Al_2O_3.B_2O_3$ | 3.00 |
| | $Na_2PO_3F$ | 1.00 |
| | $Na_2SO_4$ | 6.00 |

117 grams of the sample was heated to 950°C before being cooled and pulled at 635°C, at 40 km/hr. The fibre produced was good and there were no crystallisation problems even though the surface temperature of the fibre dropped to 510°C in the pulling process.

**Example 5**

| | Component | Mole % |
|---|---|---|
| Glass Composition | | |
| | $Na_2O$ | 31.71 |
| | CaO | 14.73 |
| | $P_2O_5$ | 36.33 |
| | $B_2O_3$ | 4.78 |
| | $SO_3$ | 9.40 |
| | $Na_2PO_3F$ | 3.00 |

99 grams of the sample was heated to 800°C before being cooled to 650°C and pulled at 40 km/hr. The fibre produced was very fine but difficult to pull and quite fragile at speed.

**Example 6**

| Glass Composition | Component | Mole % |
|---|---|---|
| | $Na_2O$ | 30.77 |
| | CaO | 14.28 |
| | $P_2O_5$ | 35.28 |
| | $B_2O_3$ | 4.64 |
| | $SO_3$ | 9.12 |
| | $FePO_4$ | 2.41 |
| | $Wa_2PO_3F$ | 0.20 |
| | $Na_2PO_3F$ | 0.20 |
| | $MnHPO_4$ | 2.06 |

200 grams of the sample was heated to 850°C before being cooled to 545°C and pulled at 40 km/hr. The fibre produced was strong and thin; there was not a problem of crystallisation, in fact the glass can be stored at 550°C for 72 hours without the onset of crystallisation.

**Example 7**

Below is an example of a wool formulation and running conditions to illustrate the differences with the monofilament examples given above.

A typical wool formulation is

| | |
|---|---|
| $Na_2O$ | 26.31 |
| CaO | 17.78 |
| $P_2O_5$ | 47.04 |
| $B_2O_3$ | 5.94 |
| MnO | 1.55 |
| $Fe_2O_3$ | 0.97 |
| NaF | 0.41 |

Solution rate, non annealed = 0.0278 $mg.cm^{-2}hr^{-1}$

Melted and refined at 1000°C.
Cooled and held at 725°C.
Bushing temperature maintained at 365°C.

Thick fibres approx 1.2mm diameter drawn through pinch rollers at 2.5 $M.mm^{-1}$ from a bushing with 6 x 6.5mm diameter holes. Fibres jet attenuated to produce a fine wool 5 -15µm diameter. The wool was sprayed with silicone oil finish during the attenuation process and collected on a stainless steel mesh conveyor. Typically, attenuated wools will have diameters of 5 to 20µm. Monofilament fibres will mostly be 20 to 50µm diameter.

**Example 8**

| | |
|---|---|
| $Na_2O$ | 31.19 mole % |
| $K_2O$ | 9.63 mole % |
| $Ag_2O$ | 2.9 mole % |
| $B_2O_3$ | 2.74 mole % |
| 2NaF | 0.66 mole % |
| $P_2O_5$ | 52.88 mole % |

Furnace at 710°C - 800°C.
Bushing at 450°C - 460°C.
4.5mm bushing holes.
50km per hour pull rate.
Good fibres.
Solution rate = 1.68 not annealed 2.28 annealed.

**Example 9**

| | |
|---|---|
| $Na_2O$ | 32 mole % |
| $K_2O$ | 10 mole % |
| $Ag_2O$ | 3 mole % |
| $P_2O_5$ | 55 mole % |

Furnace at 850°C.
Bushing at 530°C.
5mm bushing holes.
55kmph.
Good strong fibres.

**Example 10**

| | | |
|---|---|---|
| $Na_2O$ | 32 | mole % |
| $K_2O$ | 10 | mole % |
| (MgO | 4 | mole %) - added as an anti-microbial |
| $B_2O_3$ | 5 | mole % |
| $Ag_2O$ | 3 | mole % |
| $P_2O_5$ | 46 | mole % |

Furnace temperature 650°C - 730°C.
Bushing temperature 410°C - 420°C.
Bushing 5.5mm diameter.
Speed up to 100kmph.
Solution rate 0.7 annealed 1.0 non annealed ($mg.cm^{-3}.hr^{-1}$).
Very good strong reliable fibre. Very stable.

**Example 11**

| | | |
|---|---|---|
| $Na_2O$ | 36.68 | mole % |
| $K_2O$ | 8.63 | mole % |
| $P_2O_5$ | 45.09 | mole % |
| $B_2O_3$ | 5.29 | mole % |
| $Ag_2O$ | 2.59 | mole % |
| (CaO | 1.73 | mole % to attenuate solution rate! |

Furnace temperature 550°C.
Bushing 62 x 5.0mm holes.
Bushing temperature 400°C.
Speed 80kmph.
Very good fibres.
Solution rate 3.11 annealed, 3.8 non annealed ($mg.cm^{-2}.hr^{-1}$).

The fibres show excellent tensile strength, flexibility and shock resistance.

The fibres are especially suitable for industrial and plastics reinforcement controlled release (anti-microbial, anti-corrosion etc) and rapidly biodegradable applications.

**Example 12**

| | |
|---|---|
| CaO | 30 mole % |
| MgO | 20 mole % |
| $P_2O_5$ | 50 mole % |

Furnace at 1050°C.
Bushing 5.5mm holes.
Bushing temperature 700°C - 720°C.
Speed up to 80kmph.
Solution rate TBA.
Very strong fibre.

**Example 13**

| | | |
|---|---|---|
| ($K_2O$ | 5 | mole %) Trace to alter dissolution rate |
| CaO | 25 | mole % |
| $Mg_2O$ | 20 | mole % |
| $P_2O_5$ | 50 | mole % |

Furnace 1000°C.
Bushing 5.5mm.
Bushing temperature 560°C - 620°C.
Speed up to 70kmph.
Solution rate TBA.
Very strong fibre.
Anti-microbial.

**Example 14**

| | | |
|---|---|---|
| CaO | 28.5 | mole % |
| MgO | 18.5 | mole % |
| $Ag_2O$ | 3 | mole % |
| $P_2O_5$ | 50 | mole % |

Furnace temperature 1050°C - 1150°C.
Bushing 4 x 5.5mm.
Bushing temperature 700°C.
Speed 50kmph.
Solution rate TBA.
Very good, strong fibre.
Anti-microbial.

**Example 15**

| | |
|---|---|
| CaO | 30 mole % |
| MgO | 20 mole % |
| $P_2O_5$ | 50 mole % |

As Example 14 (without silver)

The fibres show excellent tensile strength, flexibility and shock resistance. These fibres are suitable for applications requiring slower release and greater tensile strength plus biodegradability. The fibres are suitable for orthopaedic implants and tissue engineering applications.

**Claims**

1. A method for forming water-soluble glass fibres, the method comprising providing a composition suitable for producing a water-soluble glass and heating said composition above the melting point of said glass to form a molten glass, cooling at least a portion of said molten glass to a pre-selected working temperature and then processing said molten glass having said working temperature into fibres.

2. A method as claimed in Claim 1 wherein said portion of said molten glass is cooled slowly to said working temperature.

3. A method as claimed in either one of Claims 1 and 2 wherein said working temperature is 50-300°C above the Tg of the glass.

4. A method as claimed in either one of Claims 1 and 2 wherein said working temperature is at least 200°C below the temperature to which the glass is initially heated.

5. A method as claimed in any one of Claims 1 to 4 wherein glass wool is formed.

6. A method as claimed in any one of Claims 1 to 5 wherein phosphorous pentoxide is used as the glass former.

7. A method as claimed in any one of Claim 6 wherein boron containing compounds are used as glass modifiers.

8. A method as claimed in Claim 7 wherein $B_2O_3$ is used as a glass modifier at a mole percentage of 15% or

less.

9. A method as claimed in any one of Claims 1 to 8 wherein said glass is a silver-ion releasing glass.

10. A method as claimed in Claim 9 wherein silver orthophosphate is added during manufacture of the glass as a source of silver ions.

# INTERNATIONAL SEARCH REPORT

Int. tional Application No
PCT/GB 98/01597

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00 C03B37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 578 023 A (CORNING INC) 12 January 1994<br>see page 4, line 20 - page 5, line 34;<br>claim 4; tables I-III | 1-6 |
| A | WO 86 04807 A (UNIVERSITY OF DAYTON, US)<br>28 August 1986<br>cited in the application<br>see claims 1-5 | 1 |
| A | WO 92 07801 A (ZIMMER INC) 14 May 1992<br>cited in the application<br>see claims 1,7,8 | 1 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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|---|---|
| 21 August 1998 | 02/09/1998 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Stroud, J |

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# INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | DATABASE WPI<br>Section Ch, Week 08<br>Derwent Publications Ltd., London, GB;<br>Class D22, AN 83-18194K<br>XP002075169<br>& JP 58 004 821 A (MITSUBISHI MINING & CEMENT CO) , 12 January 1983<br>see abstract | 1 |
| A | DATABASE WPI<br>Section Ch, Week 25<br>Derwent Publications Ltd., London, GB;<br>Class L01, AN 73-80941U<br>XP002075170<br>& JP 48 042 814 B (NIPPON SHEET GLASS CO LTD) , 1973<br>see abstract | |

1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/01597

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0578023 A | 12-01-1994 | US 5330940 A | 19-07-1994 |
| | | CA 2084471 A | 07-01-1994 |
| | | JP 6056472 A | 01-03-1994 |
| WO 8604807 A | 28-08-1986 | US 4604097 A | 05-08-1986 |
| | | AU 5518386 A | 10-09-1986 |
| | | EP 0211942 A | 04-03-1987 |
| | | JP 7005335 B | 25-01-1995 |
| | | JP 62501905 T | 30-07-1987 |
| WO 9207801 A | 14-05-1992 | US 5215563 A | 01-06-1993 |
| | | AU 658380 B | 13-04-1995 |
| | | AU 8952991 A | 26-05-1992 |
| | | CA 2094931 A | 02-05-1992 |
| | | EP 0555390 A | 18-08-1993 |
| | | JP 6504754 T | 02-06-1994 |